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Complexes of 2,6-diacetylpyridine dihydrazone with middle and late first row transition metals

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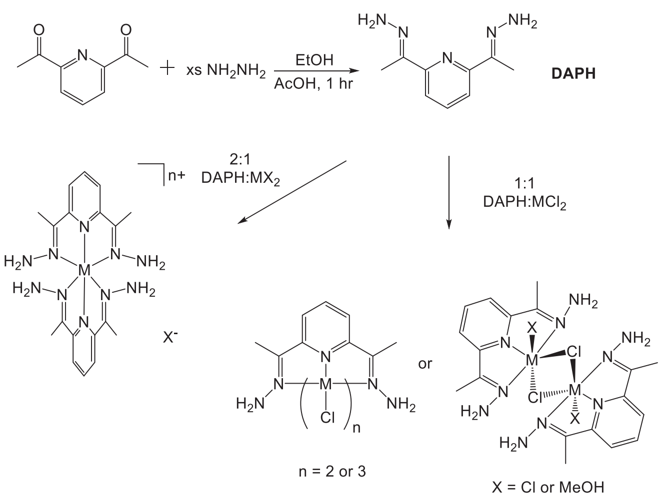
ABSTRACT

A study of the transition metal chemistry with the planar tridentate ligand 2,6-diacetylpyridine dihydrazone (**1**, DAPH) is presented, expanding the chemistry of this ligand across the first row of the transition metals. Ligand **1** forms both 1:1 and homoleptic 2:1 complexes with transition metal ions, depending on the metal salt used and reaction conditions, and seven new complexes with Mn, Fe, Co, Cu and Zn are presented. All compounds, including the ligand, have been characterized by X-ray crystallography. DAPH (**1**) binds to metal ions in an asymmetric fashion, with a M–N_{pyr} bond that is shorter than the flanking M–N_{imine} bonds. Additionally, the N_{imine}–M–N_{imine} bonds form acute angles ranging from ~140 to 160°, depending on the identity of the metal ion and ligand environment. All compounds are compared with previously elucidated DAPH structures from the literature.

Planar tridentate chelates, such as the bis(2-iminopyridyl)-isoindolines, Louie's bisiminopyridine ligands, and pincer type systems, have been explored both for their fundamental metal binding properties and as ligands for transition metal catalysts [1]. One advantage of many of these ligand systems is their ease of synthesis and ready modification at the periphery, resulting in both bulky and chiral systems that can be used as effective ligands for effecting specific organic transformations [2]. We have been working for several years on the chemistry of Schiff bases and their complexes and have turned our attention to hydrazine based ligand systems [3]. Hydrazines will react rapidly with aldehydes and ketones to generate hydrazones, which have strong affinity as ligands for transition metal ions [4,5]. The reaction of 2,6-diacetylpyridine with excess hydrazine results in a tridentate chelate shown in Scheme 1, known as 2,6-diacetylpyridine dihydrazone (**1**, DAPH). Although this ligand has been previously synthesized, its transition metal chemistry has not been greatly explored [4]. Additionally, the structure of DAPH can be considered as an analog of more sterically bulky substituted hydrazones, which have been explored as catalysts for organic transformations and polymerizations [5]. In this report, we present a study that completes the middle and late first row transition metal chemistry of DAPH, including reactions with manganese, iron, cobalt, copper and zinc, with a focus on the structures of the resultant complexes. In all cases, DAPH binds as a neutral, planar, tridentate ligand, with both 1:1 and 2:1 homoleptic ligand to metal stoichiometries.

The DAPH ligand **1** was first synthesized by Lukes and Pergal, and recently a more detailed procedure was presented by Datta and coworkers [4a,6]. The ligand can be readily prepared via the reaction of 2,6-dacetylpyridine with excess hydrazine in ethanol. Compound **1** precipitates as a pure product directly from solution, and can be used immediately in metalation reactions. We were able to grow single crystals of **1** from a diffusion of hexanes into a chloroform solution, and its structure is shown in Fig. 1. Unlike in its metal complexes (vide infra), the C–N bonds



Scheme 1. The synthesis of the metal complexes of DAPH (1).

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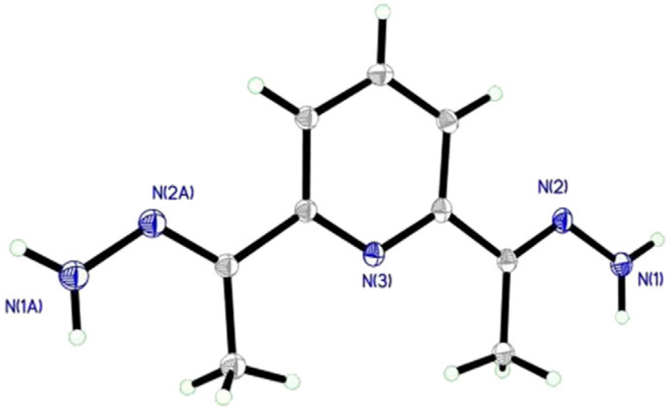

Fig. 1. The structure of **1** with 35% thermal ellipsoids.

are turned away from the central nitrogen atom. The C–N bonds of the imines measure 1.2851 (19) Å while the N–N bonds of the hydrazine units measure 1.3812 (18) Å. The hydrazine units engage in complementary hydrogen bonding with neighboring molecules in the solid state.

The chemistry of this ligand has been sporadically investigated. Early work was carried out in the 1960s with minimal characterization [7]. More recently, several compounds have been structurally characterized including Ni(II), Zn(II), Cd(II), Hg(II) and Pb(II) [4]. The DAPH ligand readily reacts with a variety of transition metal salts in methanol. Depending on the metal salts used and the ratio of ligand to metal, we could obtain 1:1 ligand:metal complexes (Fig. 2) or 2:1 ligand metal complexes (Fig. 3). Reaction of one equivalent of the DAPH ligand with $FeCl_3$, $CuCl_2$ and $ZnCl_2$ results in monomeric compounds (**2**, **3** and **4**), whereas reactions with $MnCl_2$ and $CoCl_2$ afford dimeric species (**5** and **6**). For the monomeric compounds, the remainder of the coordination sphere is occupied by chlorides, producing neutral species. For the dimeric compounds **5** and **6**, two bridging chlorides form a M_2Cl_2 diamond core; in the case of **5** two additional chlorides complete the coordination environment in apical positions, whereas in **6** the charge is balanced by an equivalent of $CoCl_4^{2-}$. For the 2:1 ligand:metal ratio reactions, homoleptic complexes **7**, and **8** are obtained, from $FeCl_2$, and $Co(NO_3)_2$ respectively. The structures of the cations for these compounds are shown in Fig. 2, and the two are similar in structure to each other and the previously elucidated Ni(II) and Zn(II) complexes [4a,b]. Since the ligand is neutral, and since the identity and number of the anions in each of the structure can be clearly determined, the oxidation states of these compounds are unambiguous. With the exception of compound **4**, all of the complexes are paramagnetic. All of the compounds exhibit divalent metals with the exception of **2**, which has a trivalent metal ion. We measured the magnetic susceptibility of all of the compounds via the Evans method (see Supplemental information) [8]. Compounds **5** and **6** are dimeric, and compound **7** has a paramagnetic anion, so their susceptibilities are not readily interpretable with a single measurement, but compounds **2**, **3** and **8** exhibit susceptibilities of 6.1, 1.7 and 4.6 BM, corresponding to spins of 5/2, 1/2 and 3/2 respectively.

In both the mono and bis DAPH complexes, the ligand binds as a tridentate, planar species. The M–N bond lengths, shown in Table 1, reveal that the $M–N_{pyr}$ bond lengths are shorter than the adjacent $M–N_{imine}$ bond lengths. Similar trends are observed in bis(iminopyridyl)isoindoline compounds and related bis(iminoazolyl)isoindoline complexes [1c,d,f, 2a–f,3c,d]. Another feature of the DAPH ligand is the acute angle formed by the $N_{imine}–M–N_{imine}$ bonds. These angles range from ~142° (compound **5**) to ~160° (compound **7**). This magnitude of this angle is affected by two parameters: the radius of the metal ion, and the degree of displacement from the tridentate chelate. Another aspect of the metal complexes of the DAPH ligand is the effect of metal binding on the imine bond lengths; due to metal to ligand backbonding effects, the C═N bond can be lengthened. Table 1 shows these metal bound imine bond lengths, and we observe a range of behavior ranging from no effective change to the

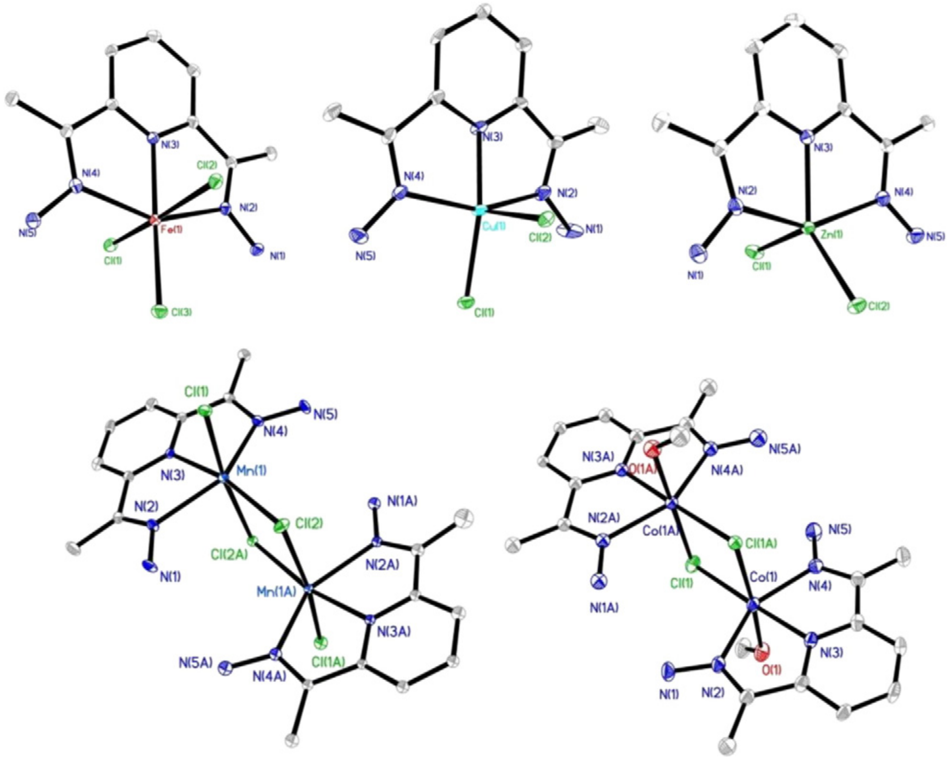

Fig. 2. The structures of compounds **2**–**6** with 35% thermal ellipsoids. Hydrogen atoms and non-coordinating anions have been omitted for clarity.